INVESTIGATION OF ORGANIC STRUCTURAL CHARACTERISTICS OF LOW-RANK COAL LITHOTYPES

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Introduction

The structural characteristics of low-rank coals and separated lithotypes were examined by several techniques. The bulk of the work was accomplished with pressure differential scanning calorimetry (PDSC). Supplemental information regarding functional groups was generated by electron spectroscopy for chemical analysis (ESCA) and infrared spectroscopy (IR). Aromaticities were calculated from the PDSC thermogram by a peak height ratio method which has been used in the past on whole coals, organic compounds, and polymers (1, 2). Aromaticities were determined for whole coals and separated lithotypes (fusain, durain, and vitrain). The fusain is the most aromatic of the lithotypes, with aromaticities ranging from 0.67 to 0.80. Calculations made using the proportions of each lithotype present in the coal determined a weighted aromaticity which corresponds very closely to aromaticity on the whole coal. ESCA was used to examine the carbon 1s peak for whole coal and lithotypes. Correlations were made between the relative abundances of C-C, C=O, and C-O bond types and coal lithotype. In nearly all cases, fusain had the largest ratio of C-C bonds. The spectral modes in the infrared which showed significant differences with lithotype include C=O and C-H stretching.

Methods and Procedures

Five low-rank coals and associated lithotypes listed in Table 1 were obtained from mines in the Fort Union and Powder River regions. The whole coals originated from channel samples representing one vertical section of the mine. Lithotypes were separated from samples taken near the location of the channel. The lithotypes were separated into three basic types based on megascopic differences. The vitrain is a very hard, vitreous lithotype. Durain has a dull, woody appearance and is soft compared to vitrain. The fusain is charcoal-like and very fragmental.

TABLE 1. COAL MINE LOCATION DESCRIPTION

Mine	Rank	County	State	Region	Seam
Beulah	Lignite	Mercer	North Dakota	Fort Union	Beulah-Zap
Indian Head	Lignite	Mercer	North Dakota	Fort Union	Beulah-Zap
Velva	Lignite	McHenry	North Dakota	Fort Union	Coteau
Glenharold	Lignite	Mercer	North Dakota	Fort Union	Scranton
Gascoyne	Lignite	Bowman	North Dakota	Fort Union	Harmon
Spring Creek	Subbituminous	Big Horn	Montana	Powder Creek	Dietz

A DuPont 1090 Thermal Analyzer system with a pressure DSC cell was used, to determine aromaticity. Details of this procedure have been published elsewhere (1, 2). Briefly, the procedure to determine the aromaticity involves hermetically sealing between 0.5 to 1.5 mg sample in an aluminum pan with a small hole punched in the

lid; the sample is then heated linearly from 150° to 600°C at 20°C/min under 500 psi oxygen to obtain the thermogram. The aromaticity is calculated from the thermogram as explained in the following section.

Samples were analyzed by transmission infrared spectrophotometry in an attempt to determine qualitative differences in functional groups among lithotypes. The dry coal spectra were obtained using KBr pellets. Appropriate amounts of coal and KBr were used to give a 0.4% or less coal to KBr mixture.

ESCA was used to determine the relative amounts of carbon as C-C, carbon bonded only to carbon or hydrogen; C-O, carbon in ether or phenol groups; and C=O, carbon in carboxyl or carbonyl groups. Samples used for ESCA analysis consisted both of ground samples and whole pieces of coal. The ground samples were pulverized to pass a 200 mesh sieve and pressed into 12.5 mm pellets using a standard laboratory press. The whole pieces of coal were attached to the sample holder with double stick tape and metal clips. Analysis was done using a Physical Electronics model 548 ESCA system. The sample bell jar was maintained at 10-100 nPa. Analysis time was approximately 30 minutes, using an analyzer pass energy of 25 eV. The x-ray beam was 5 mm in diameter to insure a large spectral area. The spectra were corrected for charging by assigning the hydrocarbon C-C peak to -284.6 eV. The spectra were resolved into components using a curve fitting routine employing a Gaussian-Lorentzian function to separate the carbon 1s peaks (3).

Results and Discussion

Aromaticities and temperatures of the peak maxima were determined for whole coals and lithotypes by the PDSC thermograms. The thermograms produced by the PDSC experiment of lithotypes from the Velva mine of North Dakota are shown in Figure 1. The apparent aromaticity, f'_a, of these samples was found by dividing the height of the high-temperature peak of the thermogram by the sum of the heights of both peaks. The corrected aromaticity, f_a, was then calculated by the empirical equation $f_a = 0.263 + 0.868\ f'_a$ (1). (Preliminary work (1) suggests that different equations for calculating f_a from f'_a may be needed for different lithotypes; however, until further data is forthcoming, the equation given above will be used.) The results show that fusain is the most aromatic while durain and vitrain have lesser but similar aromaticities. The peak temperatures of the aromatic region of the PDSC thermogram were measured to determine the amount of ring condensation (1).

Five lignites and one subbituminous coal were examined by the PDSC method. The results indicate that the fusain was consistently the most aromatic of the lithotypes. The durain and vitrain of each coal were always lower, but similar to each other, in aromaticity. The peak temperatures and corrected aromaticities of all six coals and their lithotypes are summarized in Table 2.

The temperature of the aromatic peak (high-temperature peak) is important when determining the number or average number of aromatic clusters in coal. Figure 2 is a plot of the temperature of the aromatic peak versus the number of fused rings. This plot was prepared from thermograms of model compounds and polymers of known structure containing one to five fused rings. In general, most of the compounds lie within the band bounded by straight line rising at an angle of approximately 15 degrees. The temperature of the aromatic peak has been plotted for a series of run-of-the-mine coals as a function of rank, where P is peat, L is lignite, etc. Most of the coals fall within the band depicted by the dashed lines with a slow curve upward.

TABLE 2. PEAK TEMPERATURE AND AROMATICITIES OF COALS

Sample Description	Peak Temperatures, °C Low	High	Corrected Aromaticity, f_a
Beulah (whole)	275	375	0.66
B-12 Fusain	290	390	0.88
B-12 Durain	280	365	0.66
B-12 Vitrain	295	375	0.65
Indian Head (whole)	275	360	0.68
IH-1 Fusain	280	390	0.77
IH-4 Durain	275	360	0.71
IH-4 Vitrain	280	380	0.71
Velva (whole)	285	350	0.70
V-5 Fusain	300	375	0.86
V-5 Durain	280	355	0.65
V-5 Vitrain	280	360	0.66
Glenharold (whole)	280	350	0.63
GH Fusain	270	350	0.67
GH Durain	275	345	0.62
GH Vitrain	275	345	0.63
Gascoyne Blue (whole)	380	380	0.57
GB Fusain	290	395	0.78
GB Durain	290	390	0.71
GB Vitrain	285	390	0.54
Spring Creek			
SP Fusain	297	400	0.77
SP Durain	285	400	0.69
SP Vitrain	285	400	0.74

The amount of ring condensation observed by the position of the aromatic peak in the thermograms can be determined by comparison to Figure 2. The extent of ring condensation was determined for lithotypes. The results suggest that fusain ranges from 2½ to 3½ ring clusters, durain ranges from 1 to 3½ ring clusters, and vitrain ranges from 1 to 3½. The average ring condensation for the composite samples ranges from 1½ to 2½. If vitrain and durain are considered to be derived from plant materials with little chemical alteration relative to fusain, it is reasonable to expect low values of ring condensation. Lignin would have a ring condensation number of 1, since the lignin structure is based on phenylpropane moieties. The more extreme thermal conditions which may have led to the formation of fusain would result in a greater aromatization, cross-linking, and condensation of rings.

The approximate amounts of lithotypes in the coals studied averaged 5% fusain, 40% durain, and 45% vitrain. The experimental aromaticities of the composite coals agree with values calculated from weighed aromaticities as shown in Table 3.

An example of an ESCA spectrum, for the carbon 1s region, is shown in Figure 3. The spectrum is resolved into separate peaks assigned to the C-O, C=O, and C-C bond types. The peak assignments are based on analogy to model polymers, particularly polyethylene terephthalate (3). The C-C peak was corrected to -284.6 eV to account

TABLE 3. CALCULATED VERSUS EXPERIMENTAL AROMATICITIES

Coal	Corrected Aromaticity of Lithotype			Calculated Aromaticity For Whole Coal	Calculated Aromaticity For Whole Coal
	Fusain	Durain	Vitrain		
Beulah	0.80	0.66	0.65	0.66	0.66
Indian Head	0.77	0.71	0.71	0.71	0.68
Velva	0.86	0.65	0.66	0.66	0.70
Glenharold	0.67	0.62	0.63	0.63	0.63
Gascoyne Blue	0.78	0.71	0.54	0.64	0.57

for the effects of sample charging. The ratios of individual peak intensities to the total intensity in the carbon is region are summarized in Table 4 for Beulah and Gascoyne lignites and their lithotypes. (The ratios of peak intensities to total intensities are shown because, for a series of experiments, the total intensity will vary from sample to sample depending on such factors as duration of the experiment and whether the sample is a chip or powder.) The relatively high concentration of C-C bonds in fusain as determined by ESCA is in agreement with the relatively high aromaticities of this lithotype determined by PDSC. The high aromaticity, reduced levels of oxygen functional groups, and the high proportion of oxidized (ie, C=O) functional groups among those remaining in fusain are all consistent with the concept that fusain has been exposed to severe thermal conditions at some point in the coalification process. The ratios of bond types for the composite sample of Beulah lignite are 0.37 for C=O/C-O and 0.09 for C=O/C-C; these agree fairly well with previously published values of 0.44 and 0.12 from ESCA examination of a different sample of Beulah lignite (3). However, as we have discussed elsewhere (3) it is desirable to incorporate data from several techniques or instruments before attempting to draw structural inferences.

TABLE 4. C=O, C-O, and C-C RATIOS DETERMINED FOR ESCA CARBON 1s SPECTRUM

Coal	C=O	C-O	C-C
Gascoyne (whole)	0.03	0.19	0.78
Fusain	0.07	0.03	0.90
Durain	0.04	0.15	0.81
Vitrain	0.04	0.10	0.86
Beulah (whole)	0.07	0.19	0.74
Fusain	0.09	0.05	0.86
Durain	0.05	0.16	0.79
Vitrain	0.0	0.21	0.88

The infrared spectra for the Beulah coal and lithotypes are shown in part in Figure 4. The intensity of the aliphatic C-H stretches for durain is much greater than that of fusain and the whole coal. The peak at 1700 cm^{-1} is most pronounced in the fusain spectra and appears as shoulders in the others. This peak may be assigned to carbonyl (C=O) stretching. The ESCA data indicates a higher concentration of C=O for fusain, providing qualitative agreement between the ESCA and IR data.

Conclusions

PDSC analysis of lithotype samples has shown that fusain is invariably the most aromatic of the lithotypes of these low-rank coals. Durain and vitrain have usually shown aromaticities similar to each other and significantly lower than fusain. It has been shown that experimental values obtained for the lithotypes could be weighted according to the approximate percentage of each lithotype in the coal, and a value for the whole coal could be calculated which compared quite well with the actual, experimental value. This correlation was especially significant when aromaticity values were used.

The correlations noted between the PDSC, ESCA, and IR include aromaticities and functional group analysis. The aromaticities determined by PDSC are supported by the ESCA C-C ratio, where in most cases fusain is the most aromatic. The unique features of the PDSC thermograms for vitrain are supported by ESCA data. For example, the shoulder peak at 400°C is an indication of increased aromatization. The C-C ratio from the ESCA spectra of vitrain is nearly as high as that of fusain but in the Beulah the vitrain C-C ratio was greater. The aliphatic nature of durain is shown by the aliphatic C-H stretching in the infrared spectra being relatively greater than in the spectra of the other lithotypes. High amounts of carboxyl content (C=O), supported by both ESCA and IR evidence, was characteristic of fusain.

The structural relationships of low-rank coals and associated lithotypes determined by ESCA, PDSC, and IR provides a means of examining coal aromaticities and functional groups. The techniques are relatively fast and help provide insight into the molecular "structure" of low-rank coals.

Acknowledgment

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References

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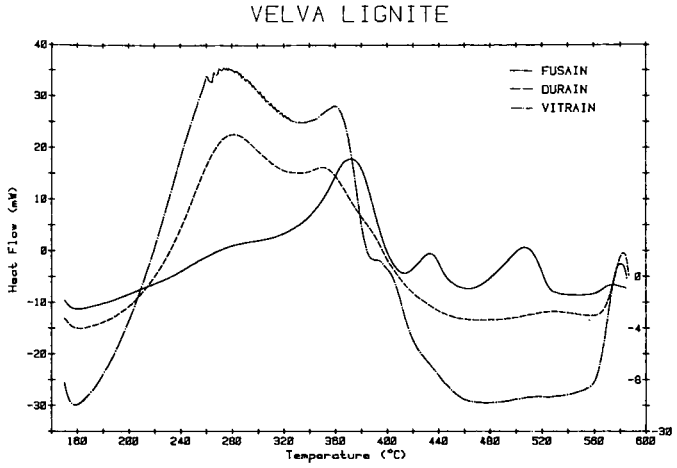

FIGURE 1. PDSC thermograms of lithotypes from the Velva, North Dakota mine.

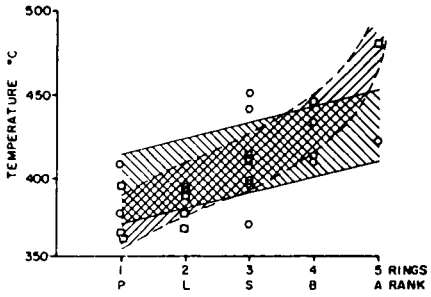

FIGURE 2. Temperature of aromatic peak as a function of number of fused rings for pure compounds (circular points; trend shown by band outlined with solid straight lines) or as a function of rank (square points; trend shown by band outlined with dashed curving lines) (1).

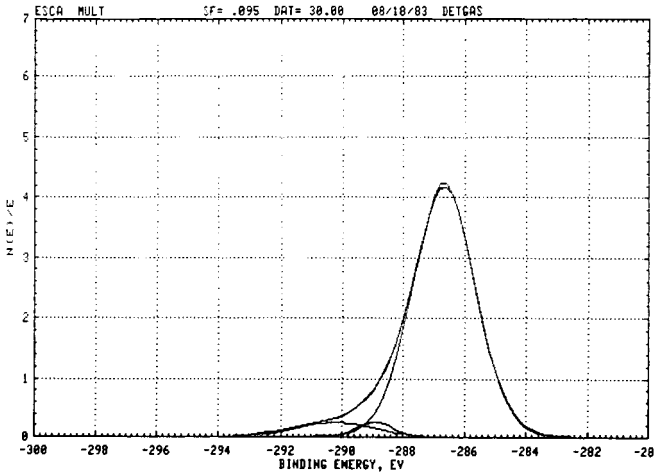

FIGURE 3. ESCA carbon 1s spectra of Gascoyne vitrain.

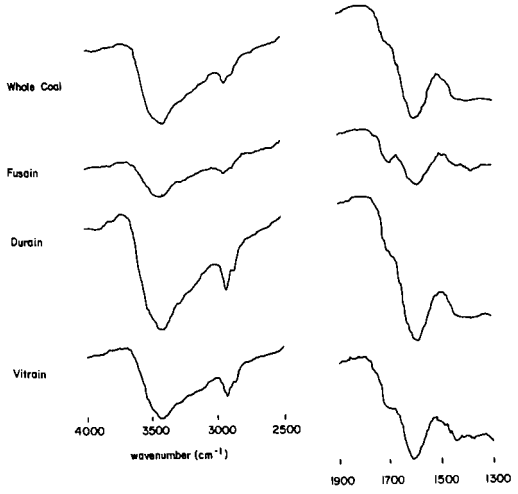

FIGURE 4. IR spectra of Beulah coal and lithotypes.